Nanostructured energetic materials using sol–gel methodologies

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Abstract

We have utilized a sol–gel synthetic approach in preparing nano-sized transition metal oxide components for new energetic nanocomposites. Nanocomposites of $Fe_2O_3/Al(s)$, are readily produced from a solution of Fe(III) salt by adding an organic epoxide and a powder of the fuel metal. These materials can be processed to aerogel or xerogel monolithic composite solids. High resolution transmission electron microscopy (HRTEM) of the dried energetic nanocomposites reveal that the metal oxide component consists of small (3–10 nm) clusters of Fe_2O_3 that are in intimate contact with ultra fine grain (UFG) ∼25 nm diameter Al metal particles. HRTEM results also indicate that the Al particles have an oxide coating ∼5 nm thick. This value agrees well with analysis of pristine UFG Al powder and indicates that the sol–gel synthetic method and processing does not significantly perturb the fuel metal. Both qualitative and quantitative characterization has shown that these materials are indeed energetic. The materials described here are relatively insensitive to standard impact, spark, and friction tests, results of which will be presented. Qualitatively, it does appear that these energetic nanocomposites burn faster and are more sensitive to thermal ignition than their conventional counterparts and that aerogel materials are more sensitive to ignition than xerogels. We believe that the sol–gel method will at the very least provide processing advantages over conventional methods in the areas of cost, purity, homogeneity, and safety and potentially yield energetic materials with interesting and special properties. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Energetic materials are substances that store energy chemically and are typically categorized as propellants, explosives, and pyrotechnics. Since the invention of black powder, over a thousand years ago, the technology for making solid energetic materials has remained largely unchanged. Their preparation typically involves either the physical mixing of solid oxidizers and fuels (e.g., black powder) to produce a composite, or the incorporation of oxidizing and fuel moieties into one molecule (e.g., trinitrotoluene, TNT) to form a monomolecular energetic material.

The basic distinctions between the composite and monomolecular approaches to obtain energetic

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materials are as follows. In composite systems, desired energy properties can be attained through readily varied ratios of oxidizer and fuels. A complete balance between the oxidizer and fuel may be reached to maximize energy density. However, due to the granular nature of composite energetic materials, reaction kinetics are largely controlled by mass transport rates between reactants. Although composites may have extreme energy densities, the release rate of that energy (power) is below that which may be attained in a kinetically controlled process, (i.e., in monomolecular energetic materials).

It is well known that the initiation and detonation properties of energetic materials are strongly influenced by their microstructural properties [1–3]. One attractive feature of the sol–gel approach to energetic material processing is that it offers the possibility to precisely control oxidizer–fuel compositions and produce materials with variable and uniform densities. In addition, it allows intimate mixing of components on the nanometer scale. All of these benefits are difficult if not impossible to achieve by most conventional procedures.

Using sol–gel chemistry it is possible to create composites whose constituents have dimensions in the nanometer range. Presumably the power of these composites will be enhanced, relative to conventional materials prepared by more traditional methods (i.e., powder mixing), because the intimate contact between components should reduce the diffusion distances between oxidizer and fuel components. This concept is not without precedent as researchers at Los Alamos National Laboratory (LANL) have shown that nano-clusters of oxidizer/fuel mixtures (with particle diameters of 20–50 nm) can achieve burn rates 1000 times that of conventional powder mixes [4–6]. These materials, called metastable intermolecular composites (MIC), rely on dynamic gas phase condensation and not sol–gel chemistry as their primary means of preparation.

In previous accounts, we described four specific sol–gel approaches for preparing energetic materials [7] and presented early results on two methods – solution crystallization and powder addition

[8]. Herein we detail our recent work on a third approach: the synthesis and physical characteristics of inorganic *energetic nanocomposites*. In these composites the fuel resides within the pores of the solid matrix while the oxidizer comprises the skeletal matrix.

Our work has focused on the development of sol–gel methods to synthesize porous monoliths and powders of nano-sized transition metal oxides (i.e., Fe_2O_3, Cr_2O_3, and NiO). When combined with oxophillic metals such as aluminum, magnesium, or zirconium these mixtures can undergo the thermite reaction (a scheme of the reaction is given below in (1)). In the thermite reaction the metal oxide ($M_{(1)}O(s)$) and oxophillic

$$M_{(1)}O(s) + M_{(2)}(s) \rightarrow M_{(1)}(s) + M_{(2)}O(s) + \Delta H$$

$$(1)$$
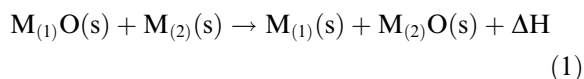
metal ($M_{(2)}(s)$) undergo a solid-state reduction/oxidation reaction, which is rapid and very exothermic; indeed, some thermite reaction temperatures exceed 3000 K. Such reactions are examples of oxide/metal reactions that provide their own oxygen supply and, as such, are self-sustaining once initiated. The energy density of these composite systems can be nearly twice that of the best monomolecular energetic materials. They have found use in a variety of processes and products including hardware destruction devices, welding of railroad track, as torches in underwater cutting, additives to propellants and high explosives, free standing heat sources, airbag ignition materials, and a host of other applications [9–18]. Traditionally, thermites are prepared by mixing fine component powders, such as ferric oxide and aluminum. Mixing fine metal powders by conventional means can be an extreme fire hazard; sol–gel methods reduce that hazard while achieving ultrafine particle dispersions that are not possible with normal processing methods. In conventional mixing, domains rich in either fuel or oxidizer can exist which limit the mass transport and therefore decrease the efficiency of the reaction. Sol–gel derived nanocomposites, however, should be more uniformly mixed, thus reducing the magnitude of this effect.

2. Experimental

2.1. Oxidizing-skeleton/fuel nanocomposites

In an earlier account, we described a sol–gel procedure for synthesizing lanthanide oxide aerogels from hydrated salts of erbium, praesodymium, and neodymium using propylene oxide as a gelation agent [19]. This synthesis approach works well for a variety of inorganic metal oxides, and we have used it successfully to make an iron-oxide oxidizing skeleton from Fe(III) salts for a nanocomposite thermite. The details and mechanism of this synthesis including the dependence of gel formation and rate on the type of epoxide used, the type of Fe(III) salt, epoxide/Fe(III) ratio, amount of water present (Fe/H_2O), along with the preferred solvent choice (i.e., polar vs. non-polar, aprotic vs. protic) has been previously described in detail [20]. Essentially, with a sufficient amount of water and epoxide, preferably in a polar protic solvent, transparent red–brown monolithic gels will form. It should be noted that the epoxide acts as a gelation agent that is consumed in the process of gel formation and not as a catalyst.

In a typical procedure, 1.0 g $Fe(NO_3)_3 \cdot 9H_2O$ (2.5 mmol) is dissolved in 5.0 g of 200 proof ethanol with stirring to give a clear red–orange solution. Upon the addition of 1.0 g of propylene oxide (17 mmol), there is a rapid exothermic reaction accompanied by a color change to a dark red–brown solution. (*Caution*: the color change is accompanied by significant heat generation that in some cases can lead to rapid boil over of the synthesis solution. The authors recommend the cautious addition of the epoxide to the Fe(III) solution in a well-ventilated lab space to remedy this problem.) Under the above conditions, gelation occurs in less than 5 min.

Powdered metal fuels, like aluminum, were added to stirred Fe(III)/epoxide solutions just before gelation to obtain the best homogeneity. Rigid wet monolithic gels with uniformly distributed aluminum particles were obtained by this approach. For the materials reported here two types of aluminum metal were used. Micron-sized (ave. diameter $\sim$6 μm) aluminum metal from

Alcan–Toyo and nanometer-sized aluminum (ave. particle diameter $\sim$30 nm) prepared by the dynamic gas condensation method at LANL were used as received. For all energetic nanocomposite formulations the molar ratio of Fe(III)/Al was 1.0 (as it is in the balanced thermite reaction).

The final step of removing the pore fluid from the wet gels is accomplished by either evaporation (in a vacuum oven held at 70°C) over 5–6 days to produce a xerogel, or by supercritical extraction (SCE) with carbon dioxide to yield a monolithic aerogel. The low temperature SCE was performed in a Polaron™ critical point drier. For this operation, the gel is placed in the drier where the liquid in the pores is exchanged with liquid CO_2 by a series of flush and drain cycles at 10°C. Following solvent exchange, the temperature of the vessel is ramped to 45°C at a rate of 0.5°C per minute, while maintaining a pressure of $\sim$100 bars. The vessel is depressurized at a rate of $\sim$ 1 bar per minute, before being purged and cooled. The time required to complete the entire exchange and extraction process for 1 cm diameter samples is typically 3–4 days.

2.2. Physical characterization

High resolution transmission electron microscopy (HRTEM) was performed on a Philips CM300FEG operating at 300 keV using zero loss energy filtering with a Gatan energy Imaging Filter (GIF) to remove inelastic scattering. The images were taken under BF (bright field) conditions and slightly defocused to increase contrast. The images were recorded on a 2×2 K CCD camera attached to the GIF.

Surface area and pore volume and size analyses were performed by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods using an ASAP 2000 Surface area Analyzer (Micromeritics Instrument Corporation). Samples of approximately 0.1–0.2 g were heated to 200°C under vacuum (10^{-5} Torr) for at least 24 h to remove all adsorbed species. Nitrogen adsorption data were taken at five relative pressures from 0.05 to 0.20 at 77 K, to calculate the surface area by BET theory.

The standard energetic material safety characterization techniques including the drop hammer, spark, and friction tests were performed on these materials. Using a type 12 drop hammer apparatus, 2.5 kg weight is dropped from a preset height onto a 35 mg pressed pellet of the material. A threshold acoustical response from diagnostic equipment determines if an explosive event occurred. Friction tests were performed by striking a ceramic stub across a portion of the material that was spread on a ceramic stage. The stub was attached to a 36 kg weight. Spark testing was performed on small amounts of the materials using an apparatus that delivered a spark with a maximum of 1 J of energy with 510 Ω resistance. The purpose of the spark test is to exceed the maximum static energy that could be generated by a person under ideal conditions (approximately 0.1 J). With all of the safety tests at least ten replicates were performed.

Differential scanning calorimetry was performed on energetic nanocomposites that were contained in pressed Al pans. The samples were heated using a TA Instruments Model 2920 differential scanning calorimeter, from room temperature to 600°C and the heating rate was 10°C/min. Powder X-ray diffraction (PXRD) experiments were performed on powdered samples mounted on quartz slides and loaded into a CPS120 Curved Position Sensitive Detector unit that utilizes CuK$_\alpha$ radiation.

3. Results

A typical HRTEM micrograph of an iron-oxide/aluminum thermite nanocomposite xerogel is shown in Fig. 1(a) and shows an interconnected iron-oxide solid skeleton with cluster sizes considerably smaller, about one order of magnitude, than the 30 nm aluminum fuel particles. The larger spherical particles in the TEM photo are the UFG aluminum, whereas the smaller particles throughout the image are the iron oxide xerogel clusters. The fuel particles tended to aggregate but intimate mixing of the fuel and the oxidizing skeleton is still observed throughout all regions interrogated, and we anticipate better homogeneity as we improve our control of gel time and mixing of fuel prior to gelation. The identities of the large spherical aluminum particles in Fig. 1(a) were confirmed by their selected area electron diffraction pattern (SAED) (Fig. 1(b)). We believe that the light colored ring around each aluminum particle is the aluminum oxide coating. It appears as though the thickness of the oxide layer is ∼5 nm.

The results of nitrogen adsorption/desorption analysis for the Fe$_2$O$_3$ oxidizing skeletons are given in Table 1. The BET surface areas for iron oxide ranged from 300 to 390 m^2/g depending on the precursor salt used in the synthesis. The results indicate that high surface area metal oxides that contain pores with nanometer-sized dimensions can be prepared by our sol–gel method.
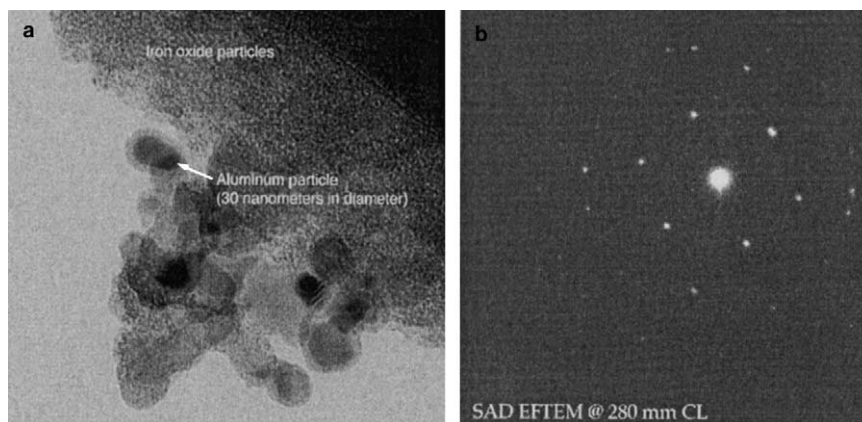

Fig. 1. (a) HRTEM of Fe$_2$O$_3$/UFG Al(s) xerogel nanocomposite and (b) SAED pattern of the labeled Al particle in (a).

Table 1
Summary of N_2 adsorption/desorption results for dry Fe_2O_3 gels made in ethanol

Gel type	Precursor salt	Surface area (BET) (m^2/g)	Pore volume (ml/g)	Average pore diameter (mm)
Xerogel	$Fe(NO_3)_3 \cdot 9H_2O$	300	0.22	2.6
Aerogel	$Fe(NO_3)_3 \cdot 9H_2O$	340	1.25	12
Aerogel	$FeCl_3 \cdot 6H_2O$	390	3.75	23

Table 2
Summary of small-scale safety tests for sol–gel derived $Fe_2O_3/Al(s)$ nanocomposites

Test	Fe_2O_3/Al (μm size)	$Fe_2O_3/UFG\ Al$	$Fe_2O_3/UFG\ Al$
	Xerogel	Xerogel	Aerogel
DH_{50}	125.6 cm	149.3 cm	89.3 cm
Spark	None at 1 J	None at 1 J	Yes at 0.03 J
Friction	None at 36 kg	None at 36 kg	None at 36 kg

Small-scale safety testing was performed on several of the materials prepared in this report the results of which are shown in Table 2. The DH_{50} value represents the height from which dropping a 2.5 kg weight will result in an explosive event in 50% of the trials. All three materials are sensitive to the drop hammer test. However, the values for all three of the materials are relatively high and indicate that none is very sensitive to impact stimuli. None of the three is friction sensitive and only the aerogel $Fe_2O_3/UFG\ Al$ sample is spark sensitive. Please note that it is spark sensitive at a test energy of only 0.03 J whereas the other materials are not even sensitive at 1 J. In light of this result, we strongly recommend that when handling the aerogel $Fe_2O_3/UFG\ Al(s)$ material procedures and conditions that minimize static electricity build up should be rigorously employed.

Differential scanning calorimetry was performed on several of the $Fe_2O_3/Al(s)$ nanocomposites that we prepared. A DSC trace from a xerogel of $Fe_2O_3/UFG\ Al(s)$ is shown in Fig. 3. One can see that the DSC is essentially featureless at temperatures less than 500°C. Above that temperature is a large exothermic peak that dominates the trace. The exotherm is centered at about 530°C and has an integrated heat of reaction of 1.5 kJ/g. The products from this DSC analysis were recovered and analyzed by powder X-ray diffraction (PXRD).

The powder pattern of the products from the DSC run shown in Fig. 3 are shown in Fig. 4, along with the known PXRD patterns for Fe(s) and two different phases of $Al_2O_3(s)$ [21]. The broad peak centered at $\sim28°$ is from the quartz slide sample holder. The poor signal to noise ratio is due to the small amount of sample used. There is good agreement, in both position and relative intensity, between the known standards and the products of the heating of the $Fe_2O_3/UFG\ Al(s)$ nanocomposite. It appears that the PXRD pattern in Fig. 4 contains diffraction peaks from a mixture of crystalline iron metal an aluminum oxide. These products are the predicted products if the nanocomposite undergoes the thermite reaction.

4. Discussion

The HRTEM and nitrogen adsorption/desorption analysis indicate the sol–gel derived oxidizer skeleton and energetic composites materials are indeed nanocomposites. It is well known, for a given bulk density, that decreasing the reactant particle size increases the combustion rate [1–3]. This was one of our primary motivations for using sol–gel methodologies. The HRTEM results given here show that small, intimately dispersed reactants are possible with this approach. The HRTEM micrograph shown in Fig. 1 also allows us to speculate on the effect that the sol–gel synthesis and processing conditions have on the aluminum fuel.

According to Fig. 1 it appears as though the thickness of the oxide layer on the Al(s) fuel is ≈ 5 nm. This is in reasonable agreement with the thickness of the oxide layer determined previously, using more rigorous methods, by the researchers at LANL [22]. This result indicates that our sol–gel processing at low solution pH does not result in significant additional oxidation of the UFG aluminum. In fact, there was very little, if any increase in the thickness of the aluminum oxide layer on the particles. The Al(s) particles were more agglomerated than we had initially assumed they would be. For an ideal nanocomposite one would like to see individual particles of UFG aluminum suspended in the nanostructured iron oxide matrix.

We are currently investigating the preparation of such a material. It is possible that techniques such as ultrasonication in a liquid suspension may help deflocculate the UFG aluminum particles. Nonetheless, the composites made by this method are readily ignited, using a thermal source, as is demonstrated in Fig. 2. This qualitative result clearly indicates these materials are energetic and that they can release that energy rapidly (i.e., have good power). To obtain more quantitative information about the reaction shown in Fig. 2 we performed detained thermal analysis of it. Analysis of the DSC trace shown in Fig. 3 indicates that the composites made here are indeed energetic. Integration of the exothermic peak in Fig. 3 resulted in a heat of reaction value of 1.5 kJ/g. This is significantly lower than the theoretical value of 3.9
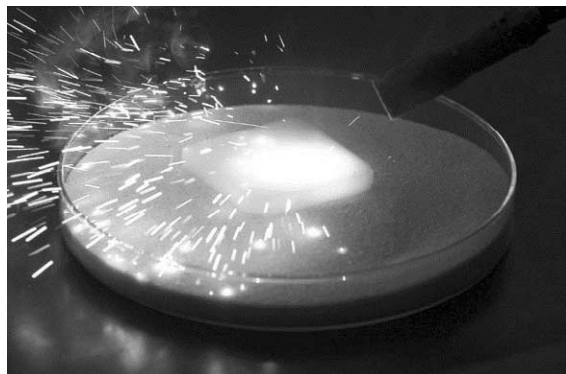

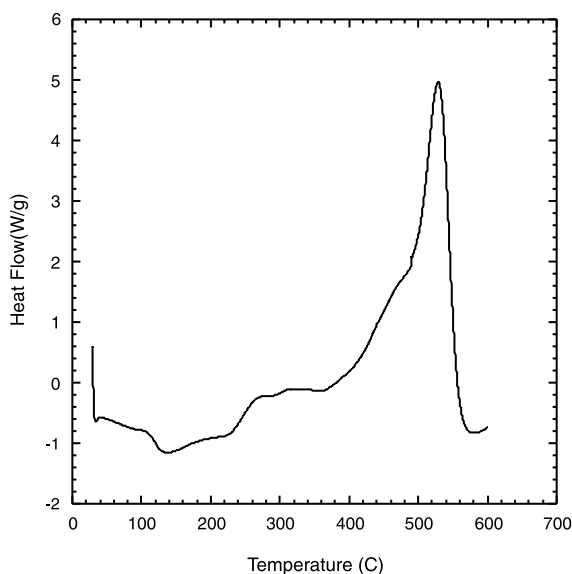Fig. 3. DSC of a xerogel Fe_2O_3/UFG Al(s) nanocomposite.

Fig. 2. Photo of the thermal ignition of an energetic nanocomposite.

kJ/g. One potential explanation involves the aluminum fuel itself. We know from HRTEM analysis that the UFG Al used in this sample has an oxide coating of ~ 5 nm. With 30 nm diameter Al this oxide coating represents a large amount of the mass of the sample. In fact, a simple calculation, based on the volume of the oxide coating, indicates that the UFG aluminum used is actually 70% Al_2O_3 weight. In addition, although the reactants are combined in quantities designed to optimize reaction stoichiometry, this assumes that all of the iron salt will be converted exclusively to Fe_2O_3. From elemental analysis we have observed that these materials have organic impurities that make up $\sim 10\%$ of the sample by mass [23]. It is likely that the impurities are due to residual solvent and/or epoxide or epoxide by-products from the synthesis. All of these facts undoubtedly contribute to a reduction in the total energy measured.

To verify that the reaction observed in Figs. 2 and 3 was indeed the thermite reaction the solid products from the DSC analysis reaction were analyzed using PXRD. The pattern of these products is shown in Fig. 4. The major constituents identified were metallic Fe and Al_2O_3, which are the expected products if the thermite reaction had occurred.
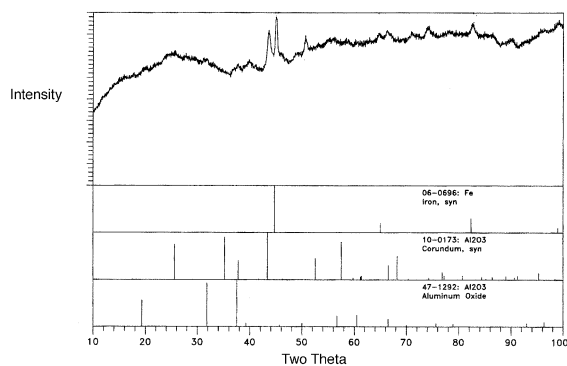
Fig. 4. PXRD pattern of the products from the DSC experiment shown in Fig. 3.

We are presently quantitatively evaluating the burn rates for a series of conventional thermite mixtures, $Fe_2O_3(s)$/UFG Al(s) energetic nanocomposites, and $Fe_2O_3(s)$/Al(s) (micron-sized) energetic nanocomposites. Although the results of these tests were not available at the time of writing, qualitatively, the $Fe_2O_3(s)$/UFG Al(s) energetic nanocomposites appear to burn much more rapidly and are more sensitive to thermal ignition than conventional thermite powders. This is not unexpected as the ignition threshold of UFG aluminum powders depends upon its physical particle morphology [22].

Not as clear however, is the observation that aerogel composites are much more sensitive to thermal ignition than their xerogel counterparts. In fact, aerogel composites made with UFG Al(s) showed spark sensitivity in small-scale safety experiments and had significantly lower drop hammer (DH_{50}) values (~150 cm for xerogels and ~90 cm for aerogel materials). More sensitive materials can be an advantage from the perspective of performance but a disadvantage in safety concerns. We believe the reason for the stark difference in reactivity between the two materials has to do with their different thermal conductivities. It is well known that the thermal conductivity of an aerogel is much lower than that of a xerogel of the same material [24]. Therefore, an aerogel composite will have a more difficult time dissipating a thermal stress than a xerogel composite. This likely results in the more rapid formation of 'hot spots' in the aerogel material, at a given temperature. Once one of the hot spots reaches the ignition point the reaction is self-propagating and the entire composite is ignited.

In spite of the above observation, sol–gel methodology offers other advantages of safety and stability in energetic material processing. For example, ambient temperature gelation and low temperature drying schemes prevent degradation, and the water-like viscosity of the sol before gelation, allows easy casting to near-net-shapes, which is preferred over the hazardous machining alternative. The commercial production of thermites, mixing and pressing sub-micron powders of iron oxide and aluminum, is particularly hazardous with a long history of accidental explosions [25,26]. Increased safety could be achieved by using an aqueous medium for the sol–gel reactions, as described in procedures we have previously reported [20]. This last point is also important from an environmental safety aspect as current large-scale production of some pyrotechnics require the use of toxic, flammable, and carcinogenic solvents like acetone, hexane, and hexachlorobenzene [27].

One final note, the sol–gel approach also allows the relatively simple incorporation of other metal oxides into the matrix to make a mixed-metal-oxide material. Dilution of the thermitic material with inert oxides such as Al_2O_3 (from dissolved $AlCl_3$ salt) or SiO_2 (from added silicon alkoxide) leads to a pyrotechnic material that is not as energetic as a pure iron(III)-oxide-aluminum mixture. We have performed such syntheses and noted that again, qualitatively, the resulting pyrotechnics have noticeably slower burn rates and are less energetic [25]. This type of synthetic control should allow the chemist to tailor the pyrotechnic's burn and spectral properties to fit a desired application.

5. Conclusions

Here we have demonstrated the use of a sol–gel method to prepare both aerogel and xerogel monoliths of Fe_2O_3/Al(s) energetic nanocomposites. Characterization has shown that these materials are made up of nanosized components, that are energetic, and undergo the traditional thermite

reaction. All quantitative and qualitative characterization indicates that the aerogel composites are more sensitive to ignition than their xerogel counterparts.

Energetic nanocomposites, with controlled oxidizer–fuel balances on the nanometer scale, are easily and reproducibly prepared using sol–gel chemistries. Microstructural control, unattainable by state-of-the-art composite processing, and precise oxidizer–fuel balance, not possible with current monomolecular synthesis, are major advantages. Essentially, sol–gel methodologies are helping bridge the gap between these two approaches. We believe that the sol–gel method will at the very least provide processing advantages over conventional methods in the areas of cost, purity, homogeneity, and safety and potentially yield energetic materials with interesting and special properties.

Acknowledgements

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